OPTIMIZATION OF EMULSION POLYMERIZATION OF STYRENE AND METHYL METHACRYLATE (MMA)

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A_s	area of one surfactant molecule taken up when adsorbed onto a surface, dm^2
A_{tot}	total surface area of latex particles, dm^2
B(V ,V)	coagulation rate coefficient of two particles of volume V and V', $Lmol^{-1}s^{-1}$
$C_{micelle}$	concentration of micelles, mol L−1
C_P	concentration of monomer in the latex particles, mol L^{-1}
C_{P_sat}	concentration of saturated monomer in the latex particles, mol L^{-1}
C_W	concentration of monomer in the water phase, mol L^{-1}
C_{pm}	heat capacity of themonomer, J/g ◦C
C_{pw}	heat capacity of water, J/g◦C
d_m	density of monomer, kg L^{-1}
d_p	density of polymer, kg L^{-1}
D_W	coefficients of diffusion for monomer in water,dm^2
e	error
[E]	concentration of desorbed radicals in aqueous phase, mol L^{-1}
F_m	rate of monomer to the reactor, mol s^{-1}
$F_{m,in}$	feed rate of inlet monomer, mol s^{-1}
G	number of radial intervals into which the particle size distribution is split
$[IM_i]$	concentration of oligomeric radicals of degree 'i' in aqueous phase, $molL^{-1}$
j_{crit}	polymerization critical degree for homogeneous nucleation
K	propagation volume growth rate per particle,Ls^{-1}
k_d	initiator decomposition rate coefficient, s^{-1}
k_{dM}	desorption of monomeric radicals from particles rate coefficient, s^{-1}
k_e^i	rate coefficient for entry of an oligomeric radical of degree 'i' into an existing particle, $Lmol^{-1}$ s^{-1}

k_{eE}	rate coefficient for re-entry of desorbed radicals, $Lmol^{-1}\ s^{-1}$
$k^{i}_{e,micelle}$	rate coefficient for entry of an oligomeric radical of degree 'i' into a micelle, $Lmol^{-1}\ s^{-1}$
k_p	long chain limiting propagation rate coefficient in the latex phase, $Lmol^{-1}s^{-1}$
k^{1}_{p}	monomeric radical propagation rate coefficient in the latex phase, $Lmol^{-1}\ s^{-1}$
$k^{i}_{p,aq}$	aqueous phase propagation rate coefficient for oligomeric radicals of degree 'i', $Lmol^{-1}\ s^{-1}$
k_{mwp}	Partition coefficient for styrene between the water phase and polymer phase
$k^{i,j}_{t,aq}$	rate coefficient for termination reaction between oligomeric radicals of degree 'i' and 'j 'in the aqueous phase, $Lmol^{-1}\ s^{-1}$
k_{tr}	radical transfer to monomer rate coefficient, $Lmol^{-1}\ s^{-1}$
M_o	monomer molecular weight, $kgmol^{-1}$
$\tilde{n}$	average number of radicals per particle
n(r)	molar concentration density of particles of unswollen radius r, $molL^{-1}dm^{-1}$
$n_o(r)$	molar concentration density of particles of unswollen radius r containing no radicals, $mol\ L^{-1}\ dm^{-1}$
$n_1^M(r)$	molar concentration density of particles of unswollen radius r, containing monomeric radicals, $mol\ L^{-1}\ dm^{-1}$
$n_1^P(r)$	molar concentration density of particles of unswollen radius r, containing polymeric radicals, $mol\ L^{-1}\ dm^{-1}$
N_A	Avogadro's constant, mol^{-1}
N_m	number of moles of monomer
$N_{m,T}$	total number of moles of monomer
N_{tot}	total number concentration of particles, L^{-1}
r	latex particle radius, dm
Δr	radial interval size, dm
<r>	number means particle radius, nm
$<r^2>$	number means squared radius, nm^2
R_P	polymerization reaction rate, mol L−1 s−1

R_{pAp}	polymerization rate of monomer A in the particle phase
R_{pAw}	polymerization rate of monomer A in water phase
r_s	swollen radius of latex particle, dm
S	concentration of added surfactant per unit volume of the aqueous phase, mol L−1
S_W	concentration of free surfactant in the aqueous phase, mol L−1
T_{reac}	reaction temperature, ◦C
V_M	monomer volume in the system, L
V_P	polymer volume in the system, L
V_r	total reaction volume, L
V_W	water volume in the system, L
X	instantaneous monomer conversion
z	critical degree of polymerization for entry

PENGOPTIMUMAN BAGI METHYL METHACRYLATE DAN STIRENA EMULSI POLIMERISASI

ABSTRAK

Karya ini mengkaji pengoptimuman bagi Stirena dan metil metakrilat (MMA) emusi polymerisasi. Satu rangka kerja yang berasaskan model bagi operasi optimum proses pengkopolimerisasi telah digunakan dalam persekitaran gPROMS dan membolehkan kita untuk meramalkan penukaran monomer maksimum. Kerumitan proses diwakili oleh model matematik untuk pengoptimuman dan kawalan. Satu model proses yang melibatkan persamaan bagi jisim dan keseimbangan tenaga menerangkan evolusi zarah dalam reaktor berkelompok dan kinetik penyebaran dikawal dimasukkan ke dalam rangka kerja pengoptimuman. Model adalah akaun untuk fizik-kimia kompleks sub-proses yang melibatkan mekanisme pembentukan partikel dengan dua titisan monomer, surfaktan, pemula dan zarahan. Menggunakan gPROMS, sistem dianalisis data, dicipta model, algoritma maju, dimanipulasi dan diplotkan berdasarkan fungsi dan data. Penentuan profil optimum untuk pembolehubah kawalan yang digunakan untuk pempolimeran emulsi stirena dan MMA yang menghasilkan penukaran dikehendaki dengan masa kumpulan tetap dan nombor tetap purata berat molekul dalam reaktor kelompok masing-masing telah dijalankan di dalam reaktor kelompok. Pengurangan masa pra-kumpulan meningkatkan Mn tetapi mengurangkan penukaran (X_n). Lebih cepat penambahan monomer ke dalam reaktor, awal pertumbuhan rantai polimer yang membawa kepada yang lebih tinggi Mn. Kenaikan suhu tindak balas akan mengurangkan M_n sejak kenaikan suhu akan meningkatkan kadar tindak balas penamatan.

OPTIMIZATION OF EMULSION POLYMERIZATION OF STYRENE AND METHYL METHACRYLATE (MMA)

ABSTRACT

This paper studies the optimization of emulsion copolymerization of Styrene and Methyl Methacrylate (MMA). A model-based framework for optimal operation of copolymerization processes was used in gPROMS environment and enables us to predict the maximum monomer conversion for a given total monomer feed over the batch time. The complexities of the process were represented by mathematical models for optimization and control. A process model involving the equations for mass and energy balance describing the particle evolution in a batch reactor and diffusion controlled kinetics is incorporated into the optimization framework. The modeling is account for complex physic-chemical sub-processes involving particle formation mechanisms with two monomer droplets, surfactants, initiator and particulates. Using gPROMS, the system analyzed the data, created models, developed algorithms, manipulated and plotted based on the functions and data. The determination of optimal profile for control variables used for emulsion polymerization of styrene and MMA that yielded desired conversion with fixed batch time and fixed number average molecular weight in batch reactor respectively were carried out in batch reactor. Reduction of the pre-batch time increases the M_n but decreases the conversion (X_n). The faster the addition of monomer into the reactor, the earlier the growth of the polymer chain leading to higher M_n. The increases of the reaction temperature will decrease the M_n since increases of temperature will increase the rate of termination reaction.

CHAPTER 1

INTRODUCTION

1.1 Background of the proposed study

Emulsion polymerization is an important industrial application. This process widely used to produce a variety of polymers of multiple uses, for examples paints, adhesives, coatings, varnishes, SBR rubber, and PVC "paste" polymers. The molecular weight distribution (MWD), polymer microstructure, glass transition temperature (T_g), particle size distribution (PSD) and particles morphology are the factors that may affect the properties of the product. In order to produce specific latex particles with certain properties, all these parameters must be included in the process design and optimization as well as control (B.Benyahia, 2010).

Emulsion polymerization is a technique leading to colloidal polymer particles dispersed in a continuous medium, most often water. It is a free radical polymerization carried out under heterogeneous conditions. The origin infinite dimensional problem can be in principle transformed to nonlinear (NLP) problem and solved by using gPROMS software (R.Paulen, 2010).

1.2 Problem Statement

Engineers always seek new ways to obtain the polymers with prescribed end-use properties with high productivities and low cost in industry. During manufacturing processes, the optimization is a way to solve the problem domain with all those goals and constraints and get the best and optimal results. Software optimization is the process of modifying a system to make some aspect of it work more efficiently or use fewer resources to lower the operation costs in the plants. In this study, gPROMS is used to build, simulate as well as optimize the model.

There is much limiting in modeling, the control of emulsion polymerization is a challenging. In polymer industry, usually manufacturers must produce their specific polymer in its final form and shape for their intended application. This study is studying the optimization of emulsion copolymerization of styrene and methyl methacrylate (MMA) in batch process. A model was developed in the gPROMS software to describe the complete patterns of the emulsion polymerization and the monomer conversion (X_n) was optimized at the end of this work.

1.3 Research Objectives

This study outlines the following objectives:

i. To determine the maximum monomer conversion of copolymerization of Styrene and MMA for a given total monomer feed over the batch time.

ii. To determine the number average molecular weight of copolymerization of Styrene and MMA for a given total monomer feed over the batch time.

1.4 Scope of Proposed Study

The purposed study is to

- Find the optimum conversion of emulsion copolymerization of Styrene and Methyl Methacrylate (MMA) at a given total monomer feed while respecting these constraints.
- gPROMS software was used to develop a model of emulsion polymerization.
- Monomers used in the polymerization process are Styrene and MMA
- The initiator used in the process is Potassium Persulfate ($K_2S_2O_8$).
- The surfactant used in the process is Sodium Decoeyl Sulfate (SDS).

1.5 Expected Outcome

The dynamic optimization problems are transformed into nonlinear programming problem (NLP) using the CVP techniques which are solved using gROMS. An emulsion copolymerization of styrene and MMA was developed in the gPROMS and the monomer conversion of copolymerization of styrene and MMA for a given total monomer feed over the batch time was determined. gPROMS was chosen as simulation tools to optimize the model as it is expected can be simulating

well with all the data without further complexity of equations. The product quality variables copolymer composition will be controlled in this work too.

1.6 Significance of Proposed Study

Molecular weight is one of the main factors which can affect an entire polymerization process as it is related to the mechanical and end use properties of the polymer itself. By maximizing the overall conversion, the downstream separation process cost can be minimized. Apart from that, this study is able to get a better design of emulsion polymerization.

Emulsion polymerization process is a technologically and commercially important synthesis process. Every annual, millions of tones of polymers are prepared by this synthesis process. It is continues to expand because of versatility of the reaction and greater realization of the ability to control the properties of the polymer latexes produced. Better design of emulsion polymerization offers great promise for the synthesis of materials. Furthermore, by optimize the molecular conversion, a better quality of product can be produced. Lastly, this study via the gPROMS work is also able be designed to consume less energy, and less cost of operating production to produce the desired product in the polymerization field in the future.

CHAPTER 2

LITERATURE REVIEW

2.1 Emulsion Polymerization Historical Review

Emulsion polymerization is a free radical initiated chain polymerization in which a monomer, or a mixture of monomers, is polymerized in an aqueous solution of a surfactant to form a product named as latex. Latex is defined as a colloidal dispersion of polymer particles in aqueous medium (Vineet, 2004). The polymer particles usually in spherical size, but they often have the morphology that will affects the end use properties deeply. The average size of the particles is from 0.05 to 5 nm in diameter. The latex produced in this process is a stable system. The charged particles cannot be recovered by ordinary separation procedures (Jr., 2007).

There are many models for emulsion polymerization in the literature. Table 2.1 lists the most comprehensive models presented in recent years (Gao & Penlidis, 2002).

Table 2.1 Models of emulsion homo-/copolymerization

Groups	Remarks	Systems
Alhamad et al.	comprehensive model (fixed pre-batch time for the seed formation in ab initio system)	Sty,MMA
Ballard	Copolymerization model for 0-1 systems	
Broadhead et al	Copolymerization model, CSTR operation, PSD , long chain branching frequency	Sty, BD
Congalidis et al	PSD, copolymerization model	MMA,sty
Coen et al.	PSD, particle number, particle size and amount of secondary nucleation	
Coen et al.	pseudo bulk kinetics included in the time evalution of particle size distribution	
Dougherty	Comprehensive model, MWD, PSD,	Sty/MMA
Dube et al.	copolymerization long-chain branching, copolymerization model, PSD, MWD	BD/AN
Forcada and Asua	Sequence length, PSD	Sty/MMA
Giannetti et al.	Reviews on PSD	
Giannetti	Copolymerization model	
Guillot	Thermodynamic aspects in copolymerization	Sty/AN
Hamielecd et.al.	Branching, crosslinking ,PSD,MWD	
Lichti et al.	Reviews on PSD, MWD	
Lin et al.	azeotropic composition, copolymerization model	Sty/AN
Mead and Poehlein	Copolymerizaiton model, PSD	Sty/MA,Sty/AN
Min and Ray	Comprehensive model, PSD, MWD	MMA
Nomura et al.	PSD,copolymerization model	MMA/sty
Penlidis et al.	CSTR reactor, PSD, MWD	PVC
Penlidis et al.	Batch reactor, PSD, MWD	VAc
Penlidis et al.	Dynamic and steady-state modeling of batch, semi-batch and CSTR reactor, PSD, MWD	
Penlidis et al.	comprehensive review, copolymerization model, PSD,MWD	PVC,VAc/PVC
Rawlings	Comprehensive model, PSD, MWD, CSTR stability	MMA, Sty, VAc
Richards et al.	An updated version of the early model of Congalidis et a., copolymerization model, no micellar nucleation assumed, MWD,PSD	MMA,MMA/Sty
Rawlings and Ray	An updated version of the early Min and Ray's model, PSD, MWD, CSTR operation, studies on CSTR oscillations	MMA
Saldivar et al.	Most recent version of Min and Ray's model, PSD, MWD, copolymerization model	MMA/Sty,Sty/α-methyl Sty,Sty/BD

Table 2.1 Continued

Storti et al.	Copolymerization model	AN/Sty/ MMA
Storti et al.	Modeling of molecular weight distribution	
Urretabizkaia et al.	Terpolymerization model	MMA/BA/VAc

The pioneer works for emulsion polymerization are done with comprehensive models, which couple kinetic models with reactor dynamics, for homo-and copolymerization. These models are presented by Liotta et al. (1998), Coen et al. (1998), Crowley et al. (2000), Gugliotta et al. (1995), Dougherty et al. (1986), Penlidis et al. (1986), Richards et al. (1989), Li and Brooks (1993), Zeaiter et al. (2002) and Alhamad et al. (2005).

Model for simulating the semibatch emulsion polymerization of styrene were developed by Li and Brooks (1993). In this model, the polymer seed particles were firstly time introduced in the reaction. The time evolution of the monomer conversion and the degree of polymerization over the whole course of the reaction were calculated in this model. Different monomer feed rates were used and a steady state in the reaction rate, under starved feed conditions, was obtained at low feed rates.

Coen et al. (1998) developed a kinetic model which incorporated all the complex competing events such as the aqueous phase propagation and termination, micellar nucleation, secondary nucleation, coagulation and diffusion, in a zero-one system. It is the recent advancement in the fundamentals of emulsion polymerization field. A detailed mechanistic dynamic model for styrene emulsion polymerization reactor was developed by Zeaiter et al. (2002). This model was used to predict the

evolution of the polymer product MWD and PSD. A system with zero-one kinetics via free-radical mechanism steps was employed. The model comprised a set of rigorously developed population balance equations to predict the monomer conversion, PSD and MWD.

Alhamad et.al. (2005) has developed a comprehensive model for emulsion polymerization process of styrene and MMA using one fixed pre-batch time for the seed formation in *ab inito* system. The mass and energy balance in considered in the transient of the system. Population balance is used to describe the particle evolution in the development of model equations. The equations also incorporated the diffusion controlled kinetics at high monomer conversion where the transient of regime from "zero one" to "pseudo-bulk" occurs. In *ab initio* emulsion polymerization, pre-batch time is needed for the seed formation and to eliminate any dissolved oxygen from the system. (Wan Ibrahim, 2011)

By using accurate kinetic models, the relationship between process variables and the product characteristics that they influence can be observe in the process easily. At the same time, their purpose can be manifold easily from time to time. It can be concluded that by using accurate kinetic modeling, time can the save. By using the software to build the model, the number of experiments can be reduced. Consequently, cost and effort in order to investigate the effects of changes can be saving too.

The end use properties of polymers are depends on the specific molecular weight averages. As a result, molecular weight is very important. Thus, maximizing

overall conversion (X_n) is very important factor to reduce the downstream separation as well as decrease the operation cost. Alhamad et al.(2005) and Wan Ibrahim (2011) both have considered maximization of M_n for emulsion polymerization of styrene and MMA for a given total amount of monomer fed to the reactor.Wan Ibrahim (2011) also considered the X_n in her work. Her result approved that decrease of pre-batch time will increase the M_n and the desired molecular weight can be achieved in shorter time. Consequently, it can increase the overall conversion. (Wan Ibrahim, 2011)

In this work, the model of Alhamad (2005) will be used for the dynamic optimization for emulsion polymerization of styrene and MMA in batch reactor. The dynamic problem with the objective function to maximize overall conversion (X_n) is considered. The X_n will be maximized for a given M_n by optimizing initiator flow rates(F_I), surfactant flow rates (F_s) and reactor jacket temperature(T_{jo}).

2.2 Properties of Styrene

Styrene is an organic compound with the chemical formula $C_6H_5CH=CH_2$. It appears as a colorless oily liquid that evaporates easily and has a sweet smell, although high concentrations confer a less pleasant odor. Styrene monomer is a basic building block of the plastic industry. It is used to make a host of downstream derivative products that go into millions of consumer goods. Primary derivatives of styrene monomer are included polystyrene, expandable polystyrene (EPS) and acrylonitrilebutadiene-styrene (ABS)/styrene-acrylonitrile (SAN) resins, styrene

butadiene (SB) latex, SB Rubber (SBR), unsaturated polyester resins (UPR), specialty polymers, co-polymers and styrene thermoplastic elastomers (TPE)(2004).

Table 2.2 Physical Properties of Styrene Monomer

Properties	
Physical State	Liquid
Color	Colorless
Molecular Weight	104.152
Boiling Point	145.2^{o}C
Freezing Point	-30.6^{o}C
Density at 25^{o}C	0.9011 g/ml
Vapor Pressure at20^{o}C	5 mmHg
Coefficient of Cubical Expansion at 20^{o}C	0.000971^{o}C^{-1}
Critical Temperature	363^{o}C
Critical Pressure	3.84MPa 557.0psia
Critical Volume	3.38 cc/g 0.0541 ft^{3}/lb

Table 2.2 (Continue)

Heat/Combustion,Liquid@25^{o}C	-1019Kcal/mol
Heat/Formation, Vapor@25^{o}C	35.23 Kcal/mol
Heat Formation, Liquid@25^{o}C	24.84 Kcal/mol
Flash Point	31.9^{o}C
Solubility at 20^{o}C	water: 0.032 wt% Alcohol:∞ Ether: ∞
saturated concentration in air at 25^{o}C	0.81 mol% 2.84 wt%
Heat/ Polymerization at 25^{o}C	16.68 Kcal/mol

(Sources: LYONDELL,(2004))

2.3 Properties of Methyl Methacrylate (MMA)

Methyl methacrylate (MMA) is an organic compound with the formula $CH_2=C(CH_3)COOCH_3$. It appears as a colorless, volatile liquid with an acrid fruity odor. The purity of commercial MMA is typically 99.9%. It contains traces of acidity as methacrylic acid (0.003% max.; specification, 0.005% max.) and water

(0.03% max.; specification, 0.05% max.). Inhibitors added for storage and transportation are usually 2–100ppm methyl ether of hydroquinone and 25–100 ppm hydroquinone, although other phenolic inhibitors, such as dimethyl tert-butylphenol, may also be used (Ms W.Dormer, 1998).

It readily polymerizes on exposure to light, heat, oxygen, ionizing radiation, or catalysts. It is used primarily to make a variety of resins and plastics, and is most often polymerized to polymethyl methacrylate, which is used to make acrylic sheets, acrylic moldings, and extrusion powders. MMA is also copolymerized with other acrylates and used to make surface coating resins, lacquers, and emulsion polymers. The chemical is used in medicine and dentistry to make prosthetic devices and as a ceramic filler or cement.

Table 2.3 Physical Properties of Methyl Methacrylate (MMA)

Properties	
Physical State	Liquid
Color	Colorless
Molecular weight	100.11
Density	0.94 g/cm^3
Vapor Density(air = 1)	3.45
Vapor Pressure at 20oC	29.33 mmHg
Melting Point	-48^{o}C
Boiling Point	100-101 ^{o}C
Viscosity at 20^{o}C	0.6cP
Flash point	2^{o}C
Specific gravity at 20^{o}C	0.945
Heat of polymerization	-138 cal/g
Vapor Pressure at 25^{o}C	40 mmHg
Solubility	• Slightly soluble in water • soluble in alcohol, ether, aceone, methyl ethyl ketone, tetrahydrofuran, hydrofuran, ester, aromatic and chlorinated hydrocarbons

(Source: (EPA)

2.4 Properties of Persulfate

Persulfate are ions or compounds with more oxygen than normal sulfates. They do not have sulfur in a different oxidation state but they contain peroxide units, where two oxygens take the place of one in a normal sulfate; the oxygen atoms are in oxidation state −1(as shown in Figure 2.1) . Persulfate is one of the common oxidizing agent used for in-situ chemical oxidation applications.. Usually it applied in the subsurface as sodium persulfate ($Na_2S_2O_8$), potassium persulfate ($K_2S_2O_8$) and ammonium persulfate $(NH_4)_2S_2O_8$

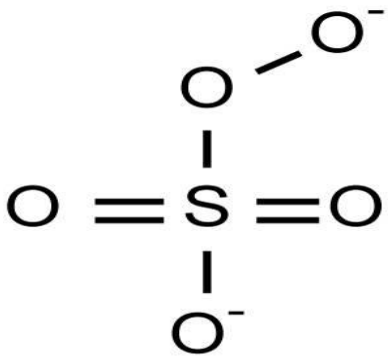

Figure 2.1 Persulfate Chemical Structure

In this study, potassium persulfate is chosen as the initiator. In chemical industries, it used for non-chlorine oxidation. It may apply in many industries. For instance, printed circuit board etching, activation of copper and aluminum surfaces, polymerization initiator, modification of starch, paper and textile cold bleaching and others. Table 2.4 showed the physical-chemical properties of Potassium persulfate.